

EMERGING TECHNOLOGY REPORT:
DESTRUCTION OF ORGANIC CONTAMINANTS IN AIR
USING ADVANCED ULTRAVIOLET FLASHLAMPS

by

Mark D. Johnson, Werner Haag and Paul G. Bylstone
Purus, Inc.
San Jose, CA 95134

and

Paul F. Daley
Lawrence Livermore National Laboratory
Livermore, CA 94550

Contract No. CR-818209-01-0

Project Officer

Norma Lewis
Emerging Technology Section, SDEB
Risk Reduction Engineering Laboratory
Cincinnati, OH 45268

RISK REDUCTION ENGINEERING LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

NOTICE

The information in this document has been funded in part by the United States Environmental Protection Agency under Contract No. CR 8 18209-01-0. It has been subjected to the Agency's peer and Administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The Superfund Innovative Technology Evaluation (SITE) Program was authorized in the 1986 Superfund Amendments: The purpose of the Program is to assist the development of hazardous waste treatment technologies necessary to implement new cleanup standards which require greater reliance on permanent remedies. A key part of EPA's effort is its research into our environmental problems to find new and innovative solutions.

The Risk Reduction Engineering Laboratory (RREL) is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

The SITE Program is part of EPA's research into cleanup methods for hazardous waste sites around the nation. Through cooperative agreements with developers, alternative or innovative technologies are refined at the bench-and pilot-scale level then demonstrated at actual sites. EPA collects and evaluates extensive performance data on each technology to use in remediation decision-making for hazardous waste sites.

This report documents Purus Inc.'s laboratory and field studies of the use of photolytic oxidation for destruction of volatile organic compounds (VOCs) in air. Field tests were performed at the Lawrence Livermore National Laboratory Super-fund site in Livermore, California on soil zones contaminated with trichloroethene

Copies of this report can be purchased from the National Technical Information Service, Ravensworth Bldg., Springfield, VA, 22161, 703-487-4600. You can also call the SITE Clearinghouse hotline at 1-800-424-9346 or 202-382-3000 in Washington, D.C. to inquire about the availability of other reports.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

This paper describes a new process for photo-oxidation of volatile organic compounds (VOCs) in air using an advanced ultraviolet source, a Purus xenon flashlamp. The flashlamps have greater output at 200-250 nm than medium-pressure mercury lamps at the same power and therefore cause much more rapid direct photolysis of VOCs, including methylene chloride (CH_2Cl_2), chloroform (CHCl_3), carbon tetrachloride (CCl_4), 1,2-dichloroethane (1,2-DCA), 1,1,1-trichloroethane (TCA), Freon 113 and benzene. The observation of quantum yields greater than unity indicate the involvement of chain reactions for trichloroethene (TCE), perchloroethene (PCE), 1,1-dichloroethene (DCE), chloroform, and methylene chloride.

TCE was examined more closely because of its widespread occurrence and very high destruction rate. Two full scale air emission control systems for TCE were constructed at Purus and tested at a Lawrence Livermore National Laboratory (LLNL) Superfund Site. The systems were operated at flash frequencies of 1 - 30 Hz, temperatures of 33 - 60 °C, flows up to 300 scfm (260 ppmv TCE) and concentrations up to 10,600 ppmv (100 scfm). Residence times ranged from 5 to 75 seconds. In all cases except at the lowest flash frequency, greater than 99% removal of TCE was observed. Careful attention was paid to product formation and mass balances. The main initial photo-oxidation product of TCE was dichloroacetyl chloride (DCAC), which upon further photolysis was converted in part to dichlorocarbonyl (phosgene or DCC) and possibly formyl chloride, and ultimately to HCl and CO_2 . Further treatment of photo-oxidation products is recommended for full-scale operation.

CONTENTS

Foreword.....	iii
Abstract	iv
List of Figures.....	vi
List of Tables	vi
Acknowledgments	vii
1. Introduction	1
2. Conclusions	3
Kinetics of VOC Photo-oxidations	3
TCE Photo-oxidation	3
Estimation of Process Parameters for Remediation	4
3. Recommendations	4
4. Experimental Methods	5
Laboratory Experiments.....	5
Field Measurements	6
5. Results and Discussion	13
Laboratory Experiments.....	13
Field Experiments.....	25
Estimation of Parameters to Achieve Recommended Treatment Levels at LLNL Site 300	28
References	30
Appendix	
Tables	
A-1 Air-2 Results.....	31
A-2 Air-3 Results.....	32

FIGURES

<u>Number</u>	<u>Page</u>
1 Lawrence Livermore Site 300 Building 834 soil venting apparatus..	7
2 Details of plumbing connections to the photoreactors	8
3 Schematic of Air-2 photochemical reactor	9
4 Schematic of Air-3 photochemical reactor	10
5 Emission spectrum for a mercury lamp vs. a xenon flashlamp.....	14
6 VOC absorbance spectra compared to xenon flashlamp spectrum.....	15
7 Photolysis plots for individual VOC's in the 208-L reactor	16
8 Photolysis plots for chloroolefins in the 208-L reactor.....	16
9 Chlorine atom scavenging with ethene in the 208-L reactor	21
10 Photolysis of TCE and 1,1-DCE as a mixture in the 208-L reactor..	23
11 Product yields from the photo-oxidation of TCE in the spectrophotometer cell.....	23
12 DCC yields from the photo-oxidation of DCAC in the spectrophotometer cell.....	24
13 Product yields from the photolysis of TCE in Air-3	26

TABLES

<u>Number</u>		
1	First order decay coefficients and wavelength-averaged disappearance quantum yields with a 2.756 kW xenon lamp	18
2	TO-14 analysis sampled on 28 Jan 1992 at 30 Hz from Air-2.	27
3	Exposure limits for TCE and its photo-oxidation products.....	28
4	Treatment parameters for 99% reduction in toxicity by UV alone at LLNL Site 300	29

ACKNOWLEDGMENTS

We thank Ken Kramasz, Bill Maxfield, Marc van den Berg, Minggong Su, and Jim of Purus, Inc. for engineering and technical support. We also thank John Greci of LLNL for his assistance during the field demonstrations. This work, in part, has been sponsored by the U.S. EPA's Emerging Technology Program (Project Officer, Norma Lewis). Although the research described in this article has been funded in part by the EPA, it has not been subject to agency review and therefore does not necessarily reflect the views of the agency and no official endorsement should be inferred.

SECTION 1

INTRODUCTION

Many environmental remediation sites suffer from pollution with volatile organic compounds (VOCs). Some of these sites are amenable to remediation by vacuum-induced soil venting and groundwater air stripping methods. However, treatment of off-gases from such operations can be problematic. Because of environmental legislation, air quality management districts require VOC air emission controls at restoration activities. Activated carbon adsorption is often utilized to control emissions. However, once breakthrough occurs, the spent carbon must be regenerated on-site or transported to the limited number of disposal or regeneration locations. In addition, this practice can be costly for sites that contain VOCs like methylene chloride or acetone with low adsorption characteristics, thereby requiring large amounts of carbon. A permanent treatment would involve complete oxidation of the VOC, so that subsequent disposal would be unnecessary. Remediation technologies that destroy VOCs on-site, such as thermal and catalytic combustion, also have limitations, particularly for sites with chlorinated VOCs.

Oxidation of organic molecules can be initiated by photolysis. Unlike thermally initiated oxidation, very little is known about the feasibility of photo-oxidation of VOCs in air as a commercial process. The lack of an intense and highly efficient light source that emits in the deep ultraviolet (<250 nm) is the reason that this has not been investigated as a process. Previously, the only light source that was routinely used for ultraviolet photolyses on a large scale was the mercury discharge lamp. Flash lamps can also be made to emit high intensities of ultraviolet light, but their use as sources for initiating photo-oxidation has previously been limited to the laboratory.

Pulsed inert-gas lamps (flashlamps) have been used for many applications including pump sources for lasers (EG&G, 1988). Lasers themselves have relatively low overall efficiency and therefore are not likely to find application in large-scale commercial or treatment processes. A flashlamp is an arc lamp that operates in the pulsed mode by alternately storing electrical energy in a capacitor and discharging it through a gas contained in a chamber of UV transmissive quartz

1988). The discharge quickly heats the gas to a very high temperature ($> 13,000$ K) and pressure, causing ionization and creating a plasma that emits light. The spectral properties of the plasma approach those of an ideal black body radiator which has a peak emission wavelength defined by its characteristic temperature. Increasing energy discharged into the plasma increases its

temperature, which lowers the wavelength of its emission maximum.

As opposed to non-specific blackbody radiation, most continuous sources emit lines that are characteristic of the electronic transitions of the unionized fill gas. For example, almost all the radiation emitted by a low pressure mercury lamp is resonance radiation of mercury vapor at 254 and 185 nm, arising from the electronic transitions $6^3P_1 \rightarrow 6^1S_0$ and $6^1P_1 \rightarrow 6^1S_0$ (Phillips, 1963). A major advantage of mercury lamps for low power applications is that they are very efficient at these two wavelengths. A disadvantage of continuous sources is that they can only be operated at relatively low intensities because the number of photons emitted is proportional to the fill gas pressure. Because the photons are in resonance with electronic transitions, they can be reabsorbed by the fill gas.

We report the application of a xenon plasma flashlamp as a UV light source for the photo-oxidation of some VOCs in air. Initially, laboratory experiments were performed on saturated and unsaturated chlorinated hydrocarbons in air to screen compounds for treatability. The kinetics of photo-oxidation were studied, and apparent quantum yields were determined for the disappearance. Efforts were made to characterize the photo-oxidation products of one of these chlorinated hydrocarbons, trichloroethene (TCE).

A full scale photoreactor was built for the photooxidation of TCE and was tested at Lawrence Livermore National Laboratory (LLNL) Site 300. This report contains a summary of the laboratory screening studies and performance data collected at the LLNL site on the photochemical treatment process for trichloroethene (TCE). The TCE destruction effectiveness and the yields of the main oxidation products were characterized under various operating conditions, including:

- * Process flow: 100 to 290 cfm
- * TCE concentration: 30 to 10,000 ppmv
- * Flash lamp frequency: 1 to 30 Hz
- * Temperature: 33-60 °C

These results, in combination with toxicological data, were used to estimate the operating conditions suitable for reducing the total toxicity from TCE and residual products by 99% using UV photolysis alone.

SECTION 2

CONCLUSIONS

KINETICS OF VOC PHOTO-OXIDATIONS

The low-wavelength emission of the pulsed xenon lamps ($\lambda_{\text{max}} = 230 \text{ nm}$) allows direct photolysis of many VOCs, particularly chlorinated compounds and freons, that was not possible with commercial mercury lamps. The quantum yields for photolyses of simple carbon-chlorine bonds are quite high, near unity. Nevertheless, light absorption by such compounds is still weak enough at 230 nm that either photosensitization or an even lower-wavelength source is needed for the photolyses to be rapid enough for commercialization at present. On the other **hand, very** rapid destruction is observed for compounds that undergo chain reactions initiated by light, notably TCE, PCE, DCE, chloroform and methylene chloride (in order). Therefore, full-scale reactors were designed for the treatment of the chloro-olefins DCE, TCE and PCE.

TCE PHOTO-OXIDATION

The initial steps of TCE photo-oxidation involve a chlorine atom propagated chain reaction (Sanhueza, et al., 1976, Blystone et al., 1991). The apparent quantum yield for this process is about 31, which makes the disappearance of TCE extremely rapid **and** efficient (Blystone et al., 1991). The main product (> 85%) from this chain photo-oxidation is dichloroacetyl chloride (DCAC). Products from the initial photolysis of TCE are insignificant because most of the products are formed via Cl atom attack.

Further oxidation of DCAC is approximately 100 times slower than the photolysis of TCE. The concentration of DCAC decays exponentially with dose, and may be a result of both direct photolysis and chlorine atom reactions. The products of further photo-oxidation after DCAC is fully formed include dichlorocarbonyl (DCC) in about 20% yield, trichloroacetyl chloride (< 2%), CHCl_3 (~0.65%), CCl_4 (~0.15%), CH_2Cl_2 (~0.05%), and possibly formyl chloride and dichloroacetic acid. The yield of DCC can be substantially enhanced by the addition of chlorine, indicating that this product may be formed by chlorine atom reaction with DCAC. At even higher light doses, DCC also decays, suggesting that the low yield is a result of its concurrent formation and destruction. Evidence was found that the carbon-containing products are eventually converted to CO_2 with enough exposure.

ESTIMATION OF PROCESS PARAMETERS FOR REMEDIATION

Although both full-scale reactors demonstrated very efficient removal of TCE, remediation of the LLNL site to toxicity level goals was not attained because of the formation of intermediate toxic products. A reduction in toxicity for TCE of 99% requires that the residual DCAC concentration be 0.026% the TCE input concentration, and the DCC concentration must be 0.45% the TCE input concentration. While it is possible to estimate the UV dose required to eliminate DCAC to this level, sufficient data does not exist to determine the dosage at which the concentration of DCC is reduced to the required level.

The maximum flow rate that meets the DCAC reduction goal under standard lamp operating conditions is between 13 and 20 cfm. At this level of treatment, the DCC concentration would still be excessive and additional treatment would be needed. Scrubbing with water under these conditions would rapidly hydrolyze the DCC to CO_2 and HCl and the DCAC to dichloroacetic acid (DCAA) and HCl. However, the accumulation of even a trace dichloroacetic acid may result in a disposal problem for the water because the expected EPA drinking water limit for DCAA is so low (-0.2 ppb; Bull R., University of Washington, personal communication, 1991).

SECTION 3

RECOMMENDATIONS

Further studies on the use of low-wavelength lamps for the destruction of VOCs should be directed at 1) examining the use of shorter-wavelength UV lamps or catalysts for photolysis of a broader range of VOCs, 2) in the oxidation of chloro-olefins, verify the effectiveness of dry or wet scrubbers for removing acidic photooxidation products, and 3) developing methods for post-treatment of products such as DCAA present in the water after scrubbing. Purus will examine some of these issues together with Argonne National Laboratory in continued demonstrations at the Department of Energy Savannah River site.

SECTION 4

EXPERIMENTAL METHODS

LABORATORY EXPERIMENTS

Chemicals

The following chemicals were used without further purification and were obtained from the following sources: from Aldrich trichloroethene 99+%, tetrachloroethene HPLC grade, **1,1,1**-trichloroethane 99%, 1,2- dichloroethane HPLC grade, dichloromethane HPLC grade, trichlorofluoromethane 99+% , dichloroacetyl chloride 99%, and chloroform HPLC grade were obtained; from Chem Service 1,1,2-trichloro- 1,2,2-trifluoroethane, and 1,1 -dichloroethene were obtained, and carbon tetrachloride AR grade was purchased from Mallinkrodt.

Dichloroacetanilide was synthesized by reaction of excess aniline with dichloroacetyl chloride in toluene. The precipitated product was filtered, washed with 0.1 M HCl, recrystallized from methanol/water, and its identity verified by GC/MS

Lamp Spectra

Flashlamp emission spectra were measured on an Oriel InstaSpec III 1024 diode-array detector fitted with a 77410 MultiSpec Grating. A Molelectron J25 pyroelectric calorimeter was used for absolute intensity determinations. Total lamp output at $\lambda < 300$ nm was measured by H_2O_2 actinometry (Nicole et **al.**, 1990).

Bench-Scale Photolyses

Photolyses were carried out in specially made 32-mL (10 cm in length, 2 cm in diameter) cylindrical quartz spectrophotometer cell, which had a Teflon stopcock sealed on one end and a threaded glass adapter sealed on the other. The threaded glass adapter was capped with a Teflon lined septum. Liquid TCE or dichloroacetyl chloride (DCAC) aliquots were injected into the cell by microliter syringe through the septum and were allowed to evaporate. The front face of the cell was then placed 4 cm from a xenon flash lamp, and the sample was irradiated. TCE concentrations were determined by drawing a sample with a gas tight syringe and directly injecting into a gas chromatograph. Acid chloride products were analyzed by derivitization with methanol, which was

injected into the cell after irradiation. Gas chromatography with electron capture or electrolytic conductivity detection was used for quantitation. DCC was analyzed by derivatization with aniline using a modification EPA method TO-6 (Winberry et al., 1990). A 2% v/v aniline/toluene solution was injected into the cell following irradiation. The solution was rinsed from the spectrophotometer cell, blown to dryness, and diluted to 1.2 mL with acetonitrile. Carbanilide, the product of the reaction of DCC with aniline, was analyzed by HPLC with UV detection at 254 nm.

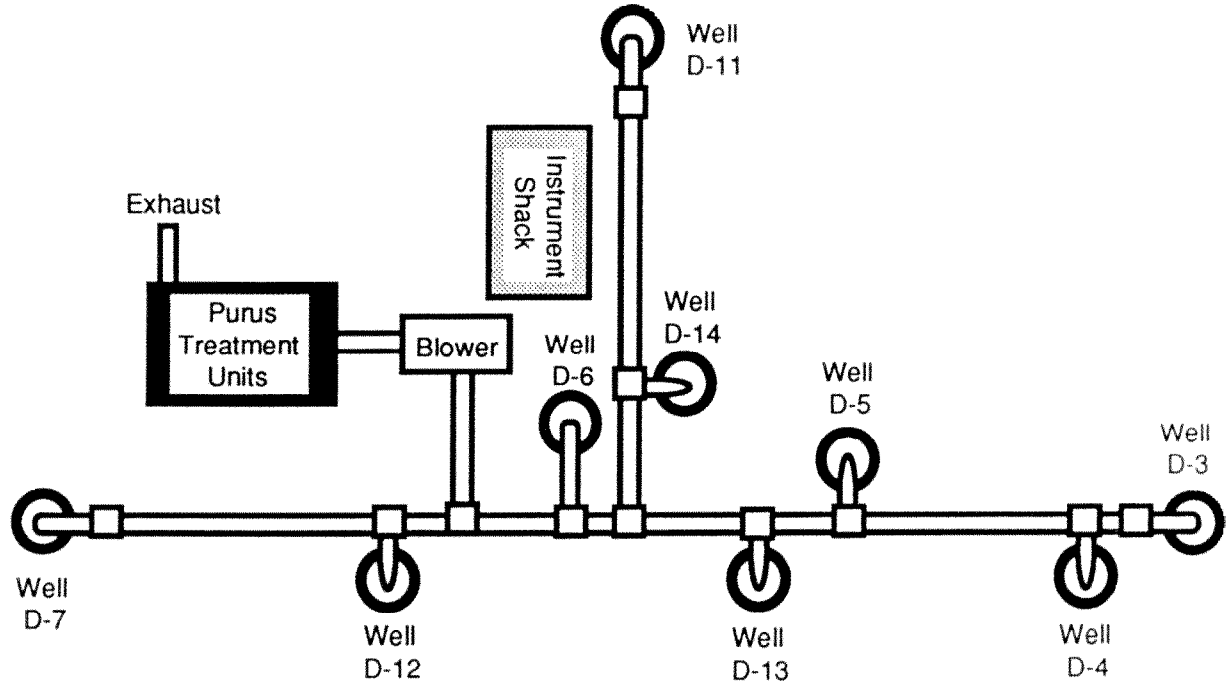
Pilot-Scale Photolyses

Air mixtures were irradiated in a 208-liter steel cylindrical reactor. A high intensity six-inch xenon flash lamp was inserted in the middle of the reactor **through** its side. The reactor contained two electric fans inside to facilitate mixing. All photolyses were performed at atmospheric pressure, and the gas temperature ranged from 300 K to approximately 340 K.

Known volumes of reagents were injected into the reactor by syringe, and were given time to evaporate and mix. Analyses of reactant concentrations were performed by gas chromatography after successive exposures of known duration. Samples were drawn from the reactor by gas tight syringe after turning off the lamp. No reaction was observed in laboratory light or in the reactor with the lamp off. Samples were directly injected into an HP5890 model 2 gas chromatograph equipped with a 30-m J&W model 624 fused silica column and using either photoionization or electron capture detection. CO₂ measurements were made in one run using a Horiba PIR-2000 CO₂ monitor.

FIELD MEASUREMENTS

Figure 1 is a schematic diagram of the Building 834 Complex chosen for the field studies at the southeast portion of Site 300 at Lawrence Livermore National Laboratory (LLNL). The process stream was pumped from the wells at Site 300 using the blower located as shown in Figure 1. Figure 2 gives details of the connections to the photoreactors. The air stream was passed through a heat exchanger to cool, and sent into two types of photoreactors (Figures 3 and 4). Air-2 is a large steel cylinder 4 feet in diameter by 8 feet in length with a volume of 101 cu. ft. Four xenon lamps are distributed about the center of the cylinder and point radially inward. The process stream flows from one end of the cylinder to the other. Air-3 is a reactor consisting of four disc shaped stainless steel chambers. Each chamber is 42 in. in diameter by 6.1 in. high with a volume of 4.1 cu. ft. exposed to the light source. The lamps in Air-3 are positioned in the center axis of each chamber. The process flow enters the bottom of each chamber, around a deflection plate, in towards the lamp, and then out the top. The chambers in Air-3 are configured



Well ID	Maximum Flow (scfm)	Maximum [TC E] (ppmv)
D3	70	420
D4	9	30
D5	15	14
D13	19	19
D14	19	10
D3, D4, D5	23	150
D3, D4, D5, D14	30	100
D13 D14	35	25
All	>250	11

Figure 1. Lawrence Livermore Site 300 Building 834 soil venting apparatus

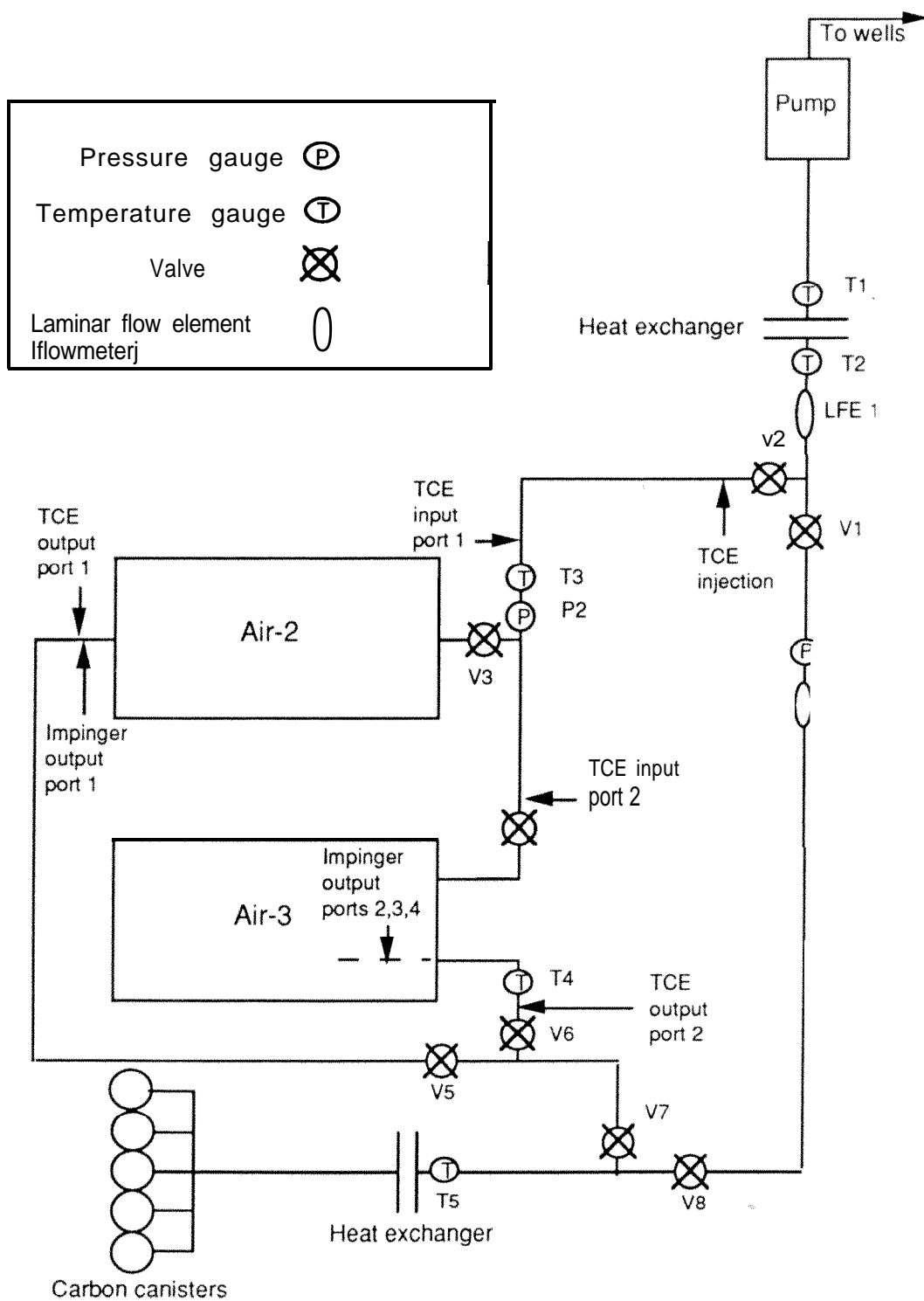


Figure 2. Details of plumbing connections to the photoreactors

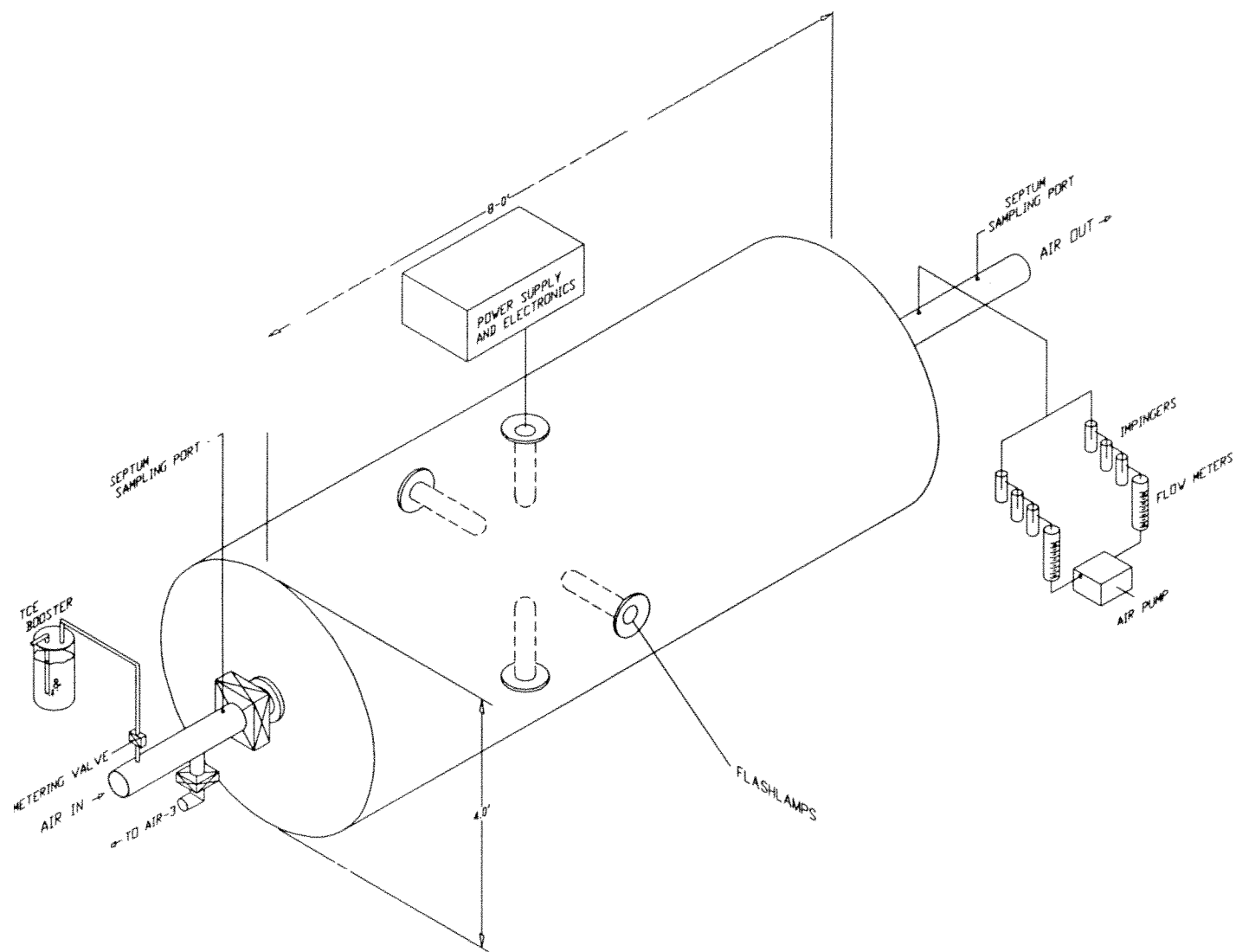


Figure 3. Schematic of Air-2 photochemical reactor

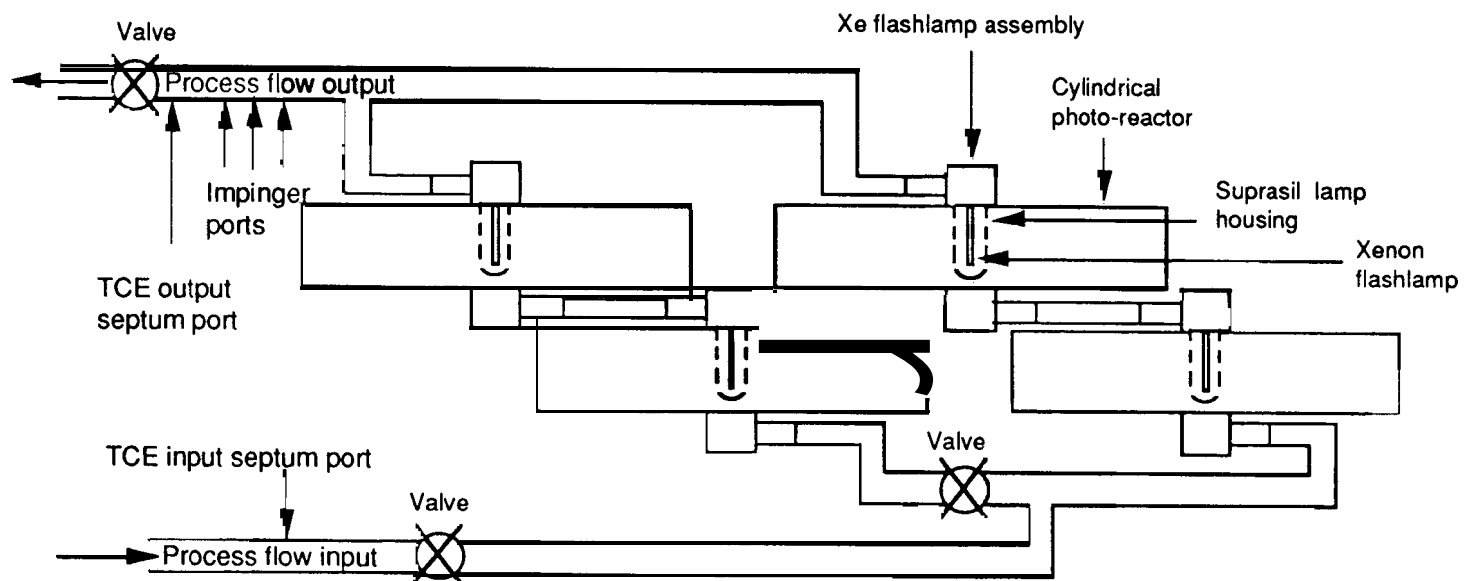


Figure 4. Schematic of Air-3 photochemical reactor

so that the flow is split through two sets of chambers in series. Some experiments were conducted with an enriched TCE air stream by gas injection from a pressurized liquid TCE-filled stainless steel bubbler before the reaction chambers.

The process flow rate was measured on LFE-2 (Figure 2), a Meriam Model 50 MC2-4 laminar flow element. Initially, the entire output from the pump was measured by closing valve V2, thus sending the entire flow around the reactors and into the carbon cans. The flow was then sent through either Air-2 or Air-3 by opening V2. Valve V1 was set so part of the flow was sent through the bypass. The flow rate through the reactors was thus the difference between the full capacity and the residual flow through the bypass when valve V1 was partly closed.

A typical sampling session involved setting the process flow rate, adjusting the TCE concentration, and alternately taking at least three input and output TCE samples while photolyzing. The impinger samples were collected during the monitoring of the TCE concentration, and were usually run for 30 minutes at a flow rate of approximately 100 mL/min. For the sampling performed in Air-2, the impingers were connected to the reactor port by 0.25 inch i.d. Teflon tubing that was split by a Teflon tee into two sets of impingers. The total length of tubing was approximately 1 meter. Even when warmed with heat tape, water tended to condense on the internal surface of the tubing, which might have prevented some of the reactive compounds from reaching the impingers. In order to minimize this problem, the impingers that were used on the tests performed on Air-3 had separate connections to the sampling ports that were less than 3 cm in length.

TCE

Trichloroethene was analyzed by gas chromatography with photoionization detection. Samples were drawn by gas tight syringe at septum sealed sample ports where the process flow entered or exited the reactor. They were injected into a Hewlett-Packard model 5890-2 gas chromatograph equipped with a 30-m J&W 624 capillary column and a photoionization detector. TCE standards were prepared in volume-calibrated glass sampling bulbs by injecting liquid TCE into the bulbs. The TCE detection limit was approximately 0.01 ppmv.

DCC

Dichlorocarbonyl was analyzed by EPA method TO-6 (Winberry et al., 1990). A small fraction of the process stream was split off through a Teflon tube into two impingers connected in series. The impingers were filled with 30 mL of a 2% v/v aniline/toluene solution, which reacts with DCC to give carbanilide. The flow was measured by a rotameter placed after the impingers

and before the pump. Volumes were determined by taking the product of the flow rate with the acquisition time. The rotameter was calibrated with a bubble flowmeter. Typical flow rates were about 100 mL/min, and typical gas volumes sampled were about 3 liters.

Samples for TO-6 analyses were evaporated to dryness at 60 °C under a stream of nitrogen and taken up in 1 or 10 mL of acetonitrile. Carbanilide was determined by high pressure liquid chromatography (HPLC) on a Perkin Elmer 410 instrument with a 15-cm octadecylsilyl column and a UV detector set at 254 nm. The eluent, a 37/63 v/v acetonitrile/water solution, was run at 0.3 mL/min. Injections of 5 μ L gave a detection limit of about 0.02 ppmv DCC, when the samples were diluted with 10 mL of acetonitrile. The average recovery of carbanilide based upon standard samples run through the blow down procedure was $106 \pm 19\%$ (95% confidence interval).

DCAC

Analyses of dichloroacetyl chloride (DCAC) for experiments in Air-2 were performed as part of the TO-6, with care taken to not blow the samples completely to dryness. Under these conditions, DCAC reacts with aniline to form dichloroacetanilide, which was measured by HPLC in the same runs as for DCC. The estimated detection limit was 0.1 ppmv DCAC. Recovery based upon standard samples run through the blow-down procedure was $104 \pm 69\%$ (95% CI). These large variations in yield were probably a result of volatilization losses, which were minimized by not blowing the samples down to complete dryness. However, this approach left some aniline in the samples, which gave a large HPLC peak and which may have given a positive error in the DCAC measurement.

For these reasons the methanol trap method was used in the subsequent testing of Air-3. Two methanol impingers were used in series, and flow rates and acquisition volumes were similar to the DCC method. The methyl dichloroacetate that formed was analyzed by gas chromatography with electrolytic conductivity detection. The detection limit for this method, for gas volumes of about 3 liters and 30 mL of methanol in each trap, was approximately 0.05 ppmv DCAC.

Chloride and Hydrolyzable Chlorine

Another impinger method was used to measure free plus the sum of all carbonyl chloride bonds, which hydrolyze in water to yield HCl. A set of three (Air-2) or four (Air-3) impingers were filled with deionized water and connected in series. Chloride was analyzed using EPA method 325.3, a titrimetric method using mercury nitrate.

VOCs

Volatile organic compounds were analyzed in one set of experiments by EPA method TO-14, a whole air sampling method (Winberry, et *al.*, 1990). The evacuated stainless steel (SUMMA) canisters, which were obtained from Coast to Coast Analytical Services, San Luis Obispo, CA, were filled during an experiment by connecting a 1 -foot long 0.25-inch OD Teflon tube to the swagelock fittings of the canister and the reactor port. Two samples were taken of the process flow with and without the lamps operating. A third sample was taken from a 20.0 ppmv standard cylinder of TCE obtained from Scott Specialty Gases. After filling, the canisters were sent to Coast to Coast Analytical Services for analysis. Agreement was reasonable; the Purus analyses agreed with the standard within 10% and the Coast to Coast analyses within 25% (see VOC results below)

SECTION 5

RESULTS AND DISCUSSION

LABORATORY EXPERIMENTS

Flashlamp Emission Spectrum

Figure 5 compares the emission spectrum of a 6-inch Purus 3675-W xenon flashlamp with that of a 7500-W medium pressure mercury lamp taken from the Peroxidation Systems, Inc. (Tuscon, AZ) literature. The data are presented as the output power integrated over the total area of the lamp and normalized to the same input power. The xenon flashlamp has a maximum at 230 nm and significant output at wavelengths as low as 200 nm, whereas the mercury lamp has most of its output at wavelengths above 250 nm. Using peroxide actinometry, we determined an overall electrical efficiency of 18.6% for generation of light below 300 nm by the Purus lamp, compared to 11.4% for the commercial Hg lamp used in UV oxidation. For the same power, the flashlamp allows a seven-fold smaller reaction chamber and thus has an advantage in capital costs. Lamp life for both lamps is on the order of 1000 hours.

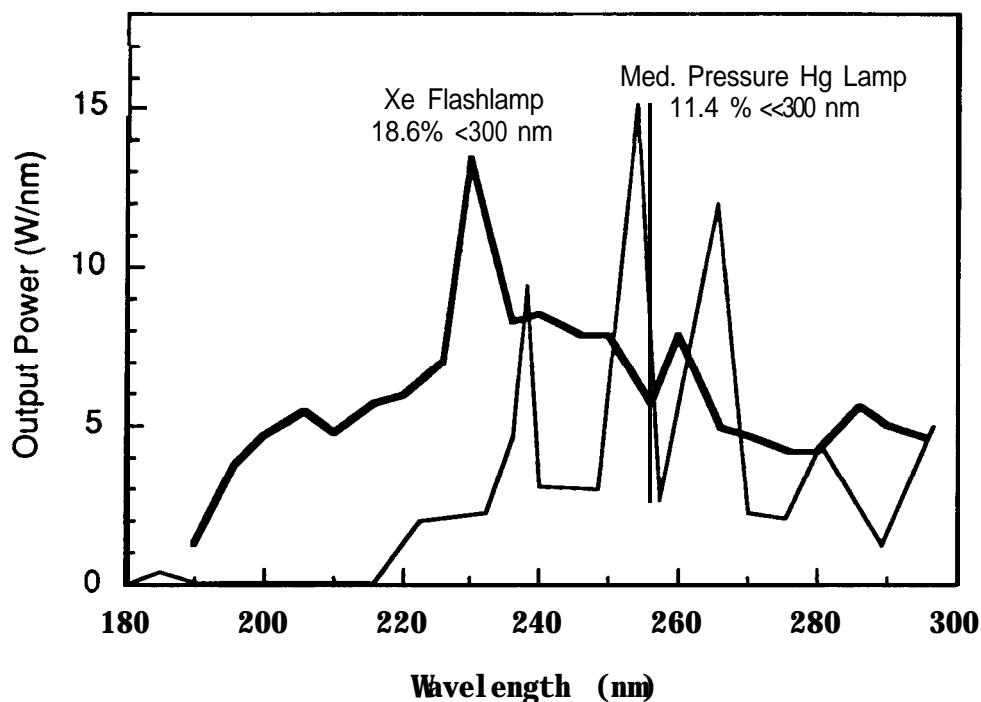


Figure 5. Emission spectrum for a mercury lamp vs. a xenon flashlamp. (All lamps corrected to 3675 W input).

Figure 6 compares the emission spectrum of the flashlamp with the absorption spectra of several VOCs (Baulch et *al.*, 1980, Hubrich and Stuhl, 1980). Note that the lamp spectrum is given on a linear scale while the absorption spectra are on a logarithmic scale. The halomethanes and TCA are weak absorbers, whereas TCE and other chloro-olefins absorb strongly in the deep UV region. The VOCs all absorb strongly below 200 nm. A shift in peak output from 254 to 230 nm is significant because it corresponds to a 1 to 2 order of magnitude increase in absorptivity of many VOCs, thereby greatly enhancing the rates of direct photolysis.

Photolysis Kinetics

At low total absorbance (~ 0.1) the direct photolysis of a compound results in the exponential decrease in concentration of the compound with photolysis time (Zepp and Cline, 1977):

$$-\frac{d[C]}{dt} = 2.3I_0\Phi\epsilon l[C] \quad (1)$$

where I_0 is the incident light intensity, Φ is the apparent disappearance quantum yield, ϵ is the molar extinction coefficient, l is the light pathlength, and $[C]$ is the contaminant concentration. For a fixed reactor size and light intensity, a simple first-order decrease in concentration of the photoreactant with irradiation time is consistent with a simple direct photoreaction. A non-exponential decay indicates that the loss of the reactant involves additional reactions whose efficiency is changing during the photolysis period.

The photolysis plots shown in Figures 7 and 8 display both exponential and non-exponential behavior. Compounds whose decay kinetics are first order include benzene, carbon

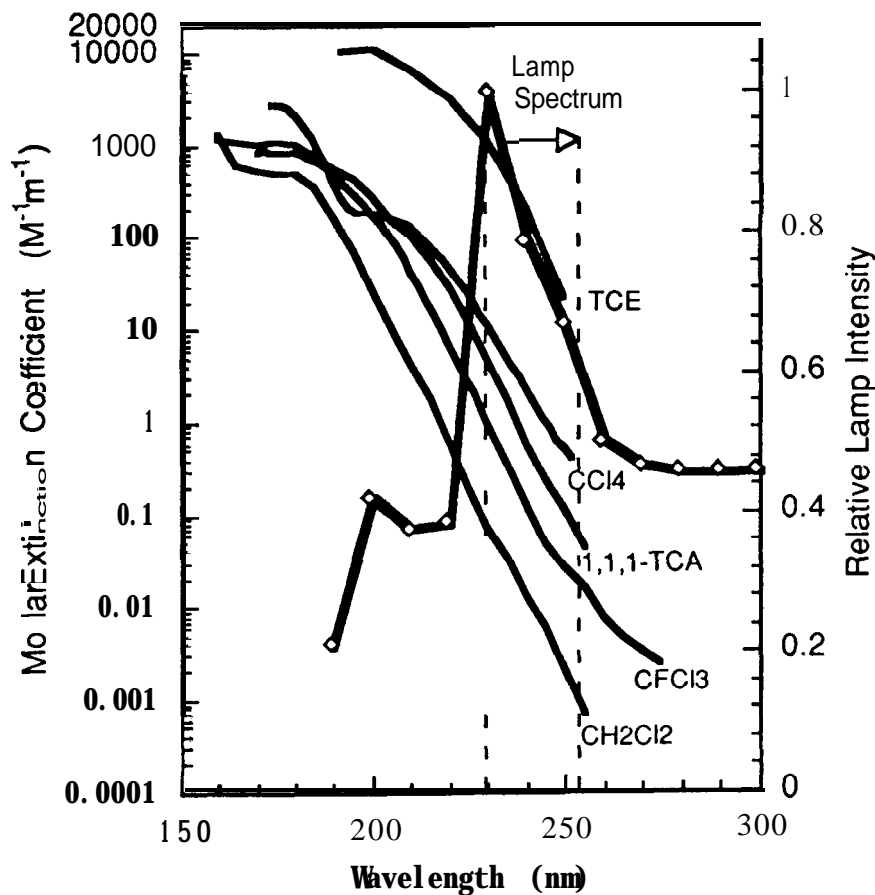


Figure 6. VOC absorbance spectra compared to xenon flashlamp spectrum.

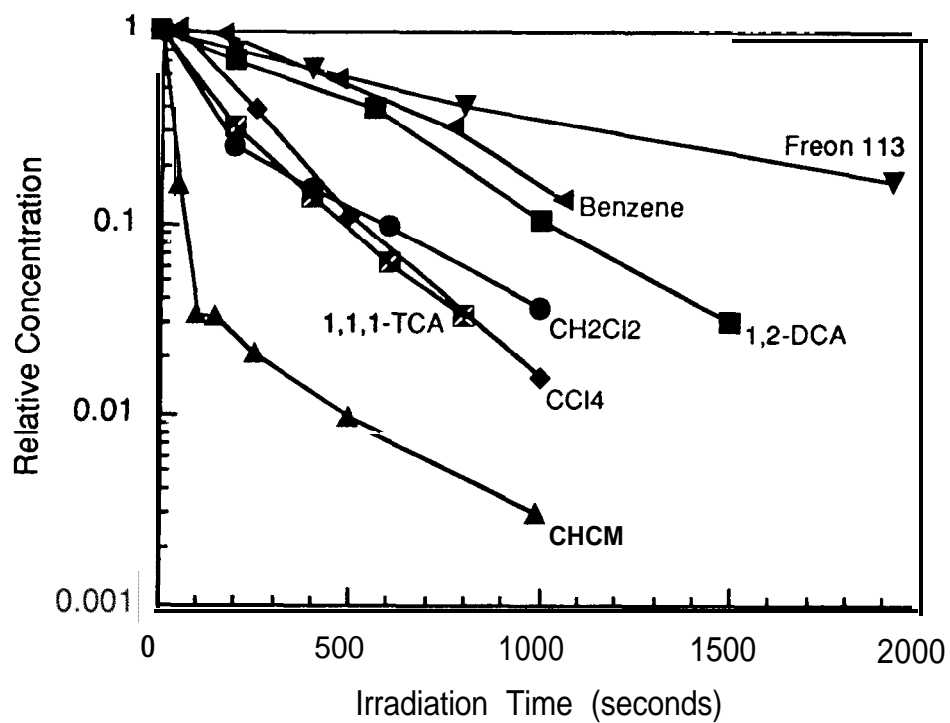


Figure 7. Photolysis plots for individual VOCs in the 208-L reactor.

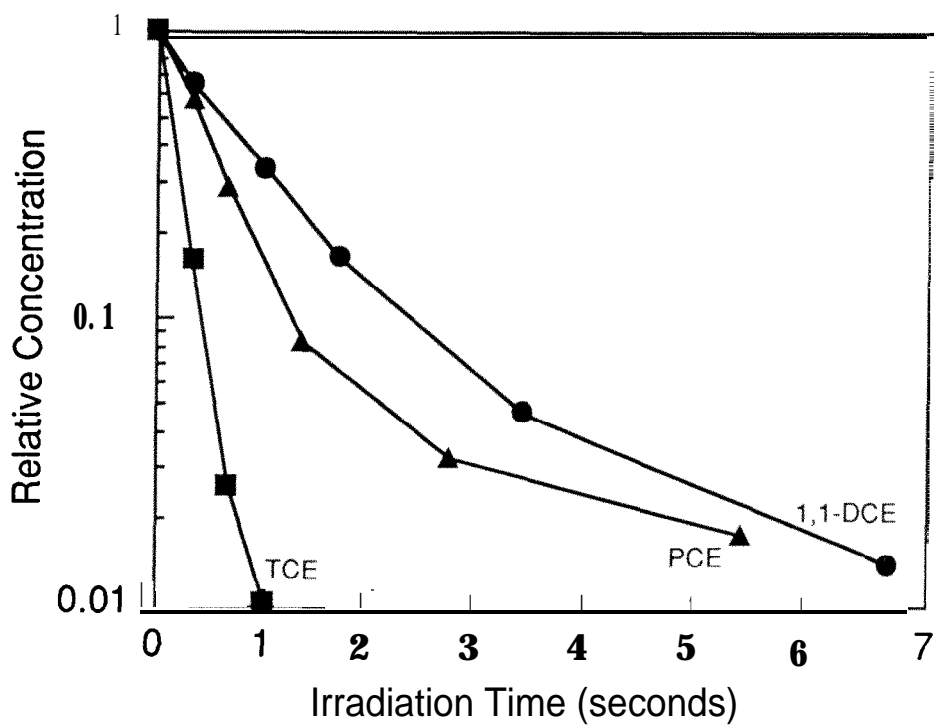


Figure 8. Photolysis plots for chloroolefins in the 208-L reactor.

tetrachloride, trichlorofluoromethane, 1,1,1-trichloroethane, 1,2-dichloroethane, and 1,1,2-trichloro- 1,2,2-trifluoroethane. Non-first order decays were observed for methylene chloride, chloroform, tetrachloroethene, trichloroethene, and 1,1 -dichloroethene. These differences in the decay behavior provide evidence that the photolysis mechanism for these sets of compounds is different.

Disappearance Quantum Yields

The magnitude of the quantum yield (Φ) for the elimination of the photoreactant also gives some mechanistic information. The ratio of the disappearance quantum yield divided by the primary yield would be unity in the case of a direct photoreaction that contains no subsequent reactions that consumes the reactant. This ratio is greater than unity when later dark reactions consume additional photoreactant, and is substantially greater than unity in the case of a chain reaction.

Table 1 shows apparent wavelength-averaged quantum yields for the compounds studied determined using carbon tetrachloride as an actinometer. From rate equation 1 for disappearance of the photoreactant in the low absorbance limit, the following expression for the quantum yield can be derived:

$$\frac{\sum I_{\lambda} \epsilon_{\lambda}^{\text{CCl}_4}}{\sum I_{\lambda} \epsilon_{\lambda}^{\text{VOC}}} \times \frac{k_{\text{VOC}}}{k_{\text{CCl}_4}} = \Phi_{\text{VOC}} \quad (2)$$

Because a broad band source was used for the excitation light, this expression incorporates the summation over the emission band of the lamp multiplied with the corresponding extinction coefficients of the compound. The disappearance quantum yield for carbon tetrachloride was taken as 1.0, based on the literature data at 214 nm (Rebbert and Ausloos, 1976). For compounds that displayed non-first order decay, the quantum yield was calculated from the initial rate determined from the first time point.

Comparison of the data in Table 1 and Figures 7 and 8 show that compounds that display non-first order decays also exhibit apparent quantum yields greater than unity. These compounds include **CH₂Cl₂**, CHCl₃, TCE, 1,1-DCE, and PCE. Furthermore, the other compounds including benzene, **CCl₄**, CFC13, 1,1,1-trichloroethane, 1,2-dichloroethane, and 1,1,2-trichloro- 1,2,2-trifluoroethane, have decays that are first order and apparent quantum yields near unity. We

TABLE 1. FIRST ORDER DECAY COEFFICIENTS AND WAVELENGTH-AVERAGED DISAPPEARANCE QUANTUM YIELDS WITH A 2.756 kW XENON LAMP

Compound	k (sec ⁻¹)*	$\frac{\sum I_{\lambda} \epsilon_{\lambda}^{\text{CCl}_4}}{\sum I_{\lambda} \epsilon_{\lambda}^{\text{VOC}}}$	x $\frac{k_{\text{VOC}}}{k_{\text{CCl}_4}}$	Apparent Φ
CCl ₄	0.00432	1.0	1.0	1.0
CCl ₂ FCClF ₂	0.00093	5.09	0.22	1.1
Benzene	0.0019	0.067	0.44	0.029
CH ₂ ClCH ₂ Cl	0.0024	N.D.#	N.D.	N.D.
CFCl ₃	0.0036	1.18	0.84	0.99
CCl ₃ CH ₃	0.0041	0.79	0.94	0.74
CH ₂ Cl ₂	0.0070	4.60	1.62	7.5
CHCl ₃	0.0366	1.79	8.47	15
1,1-DCE	1.24	0.0389	287	11
PCE	1.7	0.0134	394	5.3
TCE	5.5	0.0236	1300	31
TCE + ethene	0.075	0.0236	17	0.4

*Initial rate constants are taken for non-log-linear curves

N.D.= not determined

believe that the five compounds in this study that show non-log-linear photo-oxidation kinetics and apparent quantum yields greater than unity react by a chlorine atom chain mechanism. The other compounds are believed to react purely by direct photolysis.

The ratio of the disappearance quantum yield to that of the primary yield provides a measure of the chain length. Primary quantum yields for C-Cl bond dissociation in chloroalkanes are usually near unity (as verified for CFC13, 1,1,1-trichloroethane, and 1,1,2-trichloro-1,2,2-trifluoroethane); therefore chain lengths for methylene chloride and chloroform are approximately 8 and 15. The TCE experiment with ethene added (see below) as a **Cl•** atom scavenger suggests the primary quantum yield for TCE is near 0.4, which in turn yields a chain length of about 75.

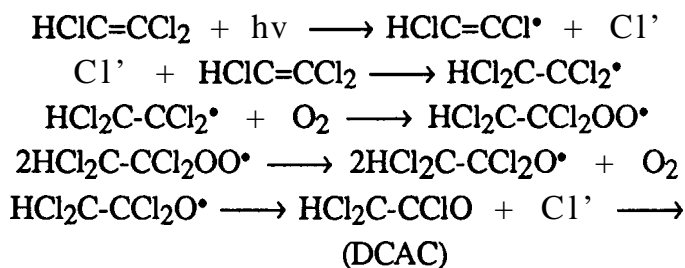
Chain Photo-oxidation Mechanism

Heicklen and co-workers have found that chain induced photo-oxidation occurs for chloroform and all of the chlorinated ethenes except vinyl chloride (Sanhueza, et **al.**, 1976)

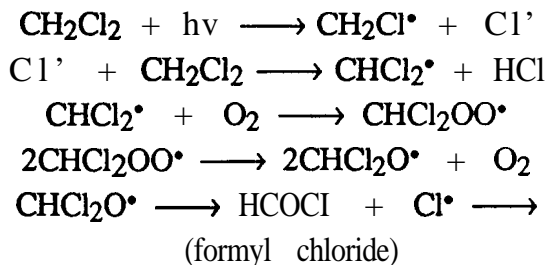
Although the reactions in their studies were initiated by Cl_2 sensitization as opposed to direct photodissociation, similar chain propagation steps should occur in both cases. Because most of the oxidation takes place in the chain steps, the types of products formed are essentially independent of whether the chain is initiated by direct photolysis or Cl_2 photolysis. In the case of TCE, the main carbon containing products were shown to be dichloroacetyl chloride (DCAC), dichlorocarbonyl chloride (CCl_2O), and carbon monoxide (Sanhuenza et al., 1976). Chloroform, carbon tetrachloride, and dichloroethylene oxide were also identified but at much lower yields (Huybrechts and Meyers, 1966). Adopting their mechanisms as the most probable, we propose the following mechanisms for VOC photo-oxidation in air:

The pathways for photo-induced chain reactions are consistent with the observed decrease in efficiency as the reactant concentration drops, because the fourth steps have a second order dependence on the concentration of the peroxy radical intermediate. As their concentration drops, they become more likely to react in other ways that do not regenerate Cl^\bullet .

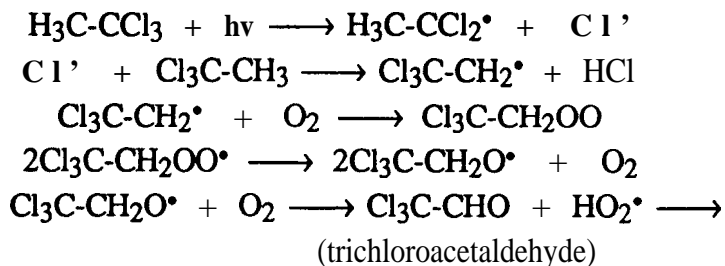
TCE Photo-induced Chain Reaction



CH_2Cl_2 Photo-induced Chain Reaction



TCA Non-chain Photolysis



A common feature of the mechanisms for TCE and methylene chloride is that Cl^\bullet atom reacts with them to generate a carbon-centered radical that has chlorine substitution. These carbon-centered radicals are then oxidized in two steps to alkoxy radicals that can then cleave a Cl^\bullet atom and propagate the chain. By contrast, the carbon radical formed from TCA has no chlorine substitution and upon oxidation it can only cleave HO_2^\bullet instead of Cl^\bullet . HO_2^\bullet is a much less reactive radical and engages predominantly in termination steps with itself and other radicals. All the compounds listed in Table 1 fit this general rule, with the exception of 1,2-DCA. 1,2-DCA appears to deviate from the rule because it gave first-order photo-oxidation kinetics, but the quantum yield is yet undetermined and may still prove to be greater than one. Cl^\bullet atoms do not react with C-Cl or C-F bonds and therefore freons and perchloroalkanes will not form a chain.

Photolysis of Chloro-olefin Mixtures

As a further test of the occurrence of a chain reaction with TCE, we photolyzed TCE in the presence of a 500-fold molar excess of ethene as a Cl^\bullet atom scavenger. Because ethene contains no chlorine, it cannot propagate a Cl^\bullet atom chain. Figure 9 and Table 1 show that the ethene decreased the TCE photolysis rate by a factor of about 75. Moreover, the rate constant in the absence of ethene decreased with time until at very long times ($[\text{TCE}] \ll \text{ppmv}$) it approached the rate constant in the presence of ethene (data not shown). Under both of these conditions chain propagation is inefficient and therefore we believe that the reaction observed in these cases is predominantly direct photolysis.

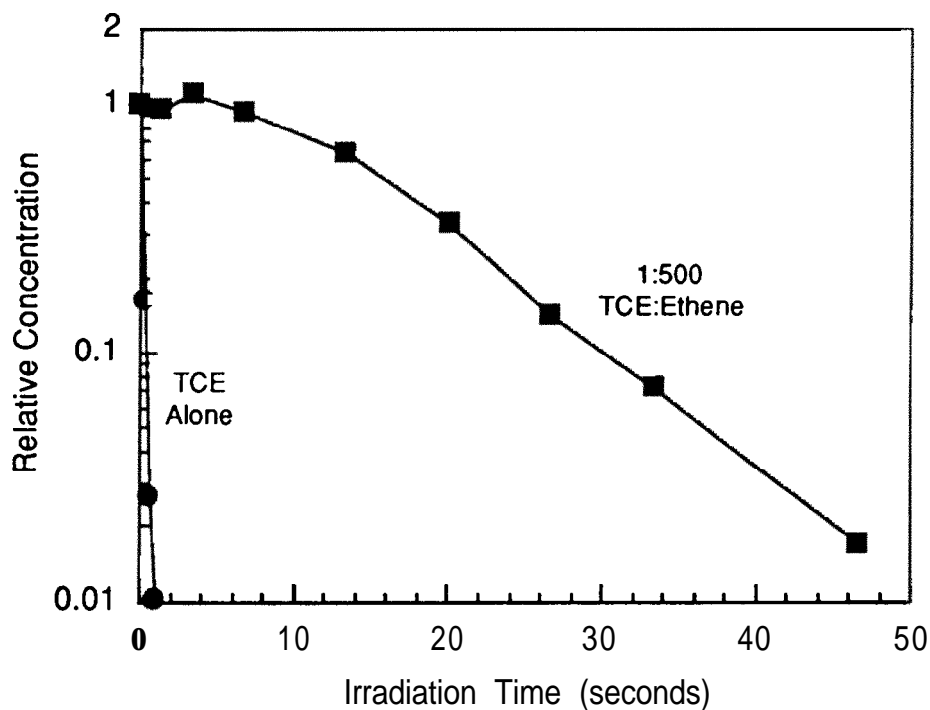
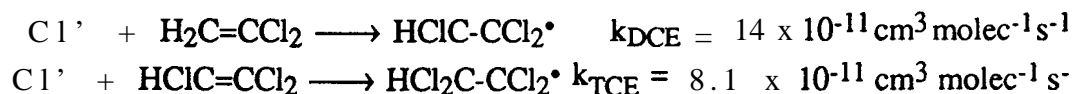


Figure 9. Chlorine atom scavenging with ethene in the 208-L reactor

Figure 10 shows a photolysis experiment with an equimolar mixture of TCE and 1,1-DCE. Comparing these results with those presented in Figure 8 shows that in the mixture the rate of TCE loss is slightly reduced but the rate of 1,1-DCE loss is considerably enhanced. We interpret this to be a result of photo-initiation predominantly by TCE because it absorbs UV light more strongly, but with chain propagation predominantly by 1,1-DCE because it reacts with chlorine atoms more rapidly (Atkinson and Aschmann, 1987):



When chains are long compared to the primary photolysis event, the relative rates of loss of 1,1-DCE and TCE should be in the same ratio as their Cl^\bullet atom reaction rate constants of $14/8.1 = 1.7$. This value is in good agreement with the observed ratio of rates of 1.5 and presents further evidence that Cl^\bullet atom is the rate-limiting oxidant in the system.

The experiments with olefin mixtures demonstrate that co-contaminants can cause both

sensitization and inhibition of photolysis. Increasing chlorine substitution on the olefin results in stronger light absorption and thus more rapid chain initiation. On the other hand, greater chlorine substitution decreases the rate of the propagation reaction with $\text{Cl}\cdot$ atom thereby reducing chain length. Finally, as chlorine substitution decreases, the statistical chance of regenerating a free $\text{Cl}\cdot$ atom and propagating a chain drops sharply. Thus, TCE and PCE can be expected to sensitize the photo-oxidation of the dichloroethene isomers and vinyl chloride because the former are better light absorbers and the latter react with $\text{Cl}\cdot$ atom more readily. However, addition of chloroolefins will not sensitize the photoreactions of the chain promoters chloroform and dichloromethane, because the chloroolefins enhance the rate of $\text{Cl}\cdot$ atom scavenging as well as production. In principle, any chlorocarbon that photolyzes to form $\text{Cl}\cdot$ atom can be expected to sensitize the oxidation of another hydrocarbon, although the effect will be small if a chain reaction is not sustained or the reaction rate constant between $\text{Cl}\cdot$ atom and the hydrocarbon is low compared to that between $\text{Cl}\cdot$ atom and its precursor.

Photo-oxidation Products of TCE

Some products of the photo-oxidation of TCE in air were investigated by irradiating TCE in a Teflon-sealed, quartz spectrophotometer cell, to allow efficient collection of the reactive products. Methanol was injected into the cell following irradiation, which derivatized the main oxidation product DCAC to methyl dichloroacetate (MDCA). Analysis by GC/MS of the methanol solution revealed that at low UV doses, DCAC (measured as MDCA) was formed at a yield exceeding 90 mole % from TCE. The identity of MDCA peak was verified by mass spectrometry. Trichloroacetyl chloride (measured as methyl trichloroacetate) was also identified by GC/MS but the yield was < 2% of the DCAC yield based on the relative ion signal. Further photolysis of TCE in air revealed an approximately exponential decrease in the DCAC concentration (Figure 11). The pattern of the TCAC concentration suggests that it is formed from DCAC but then also photolyzes.

DCAC Photo-oxidation

Because the main intermediate product from TCE photo-oxidation is dichloroacetyl chloride, subsequent products are largely determined by the photochemistry of DCAC. One product formed from the photo-oxidation of DCAC is DCC, as shown in Figure 12. Note that these experiments were conducted by starting with DCAC instead of TCE in the spectrophotometer cell, and measuring the yield of DCC in the absence and presence of added Cl_2 gas. The DCC

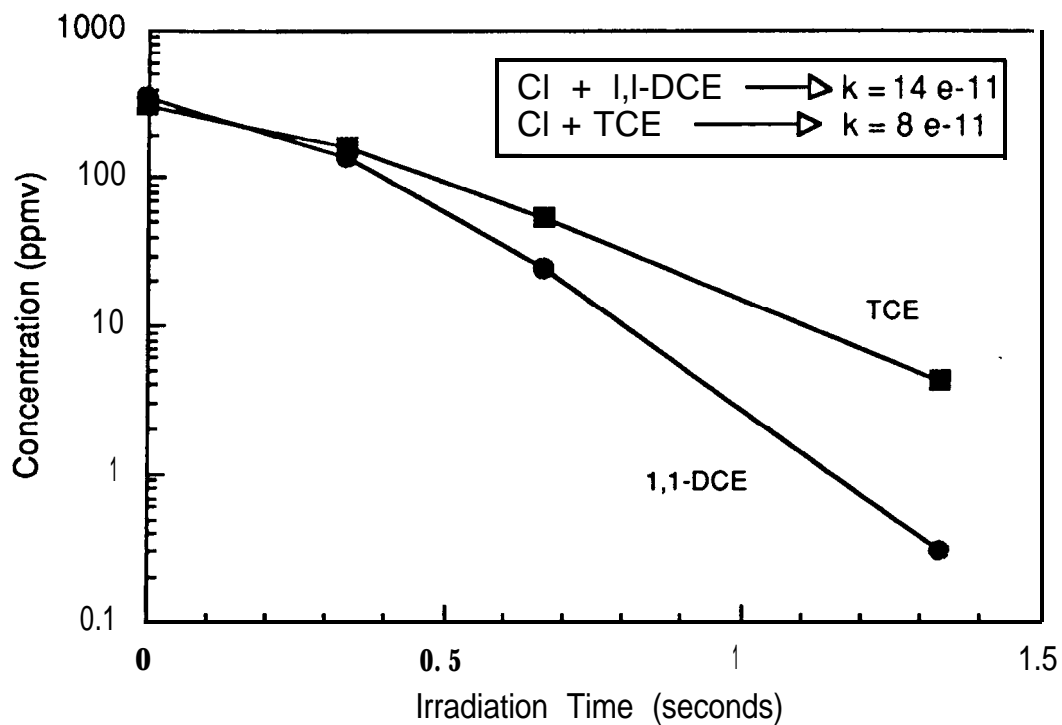


Figure 10. Photolysis of TCE and 1,1-DCE as a mixture in the 208-L reactor

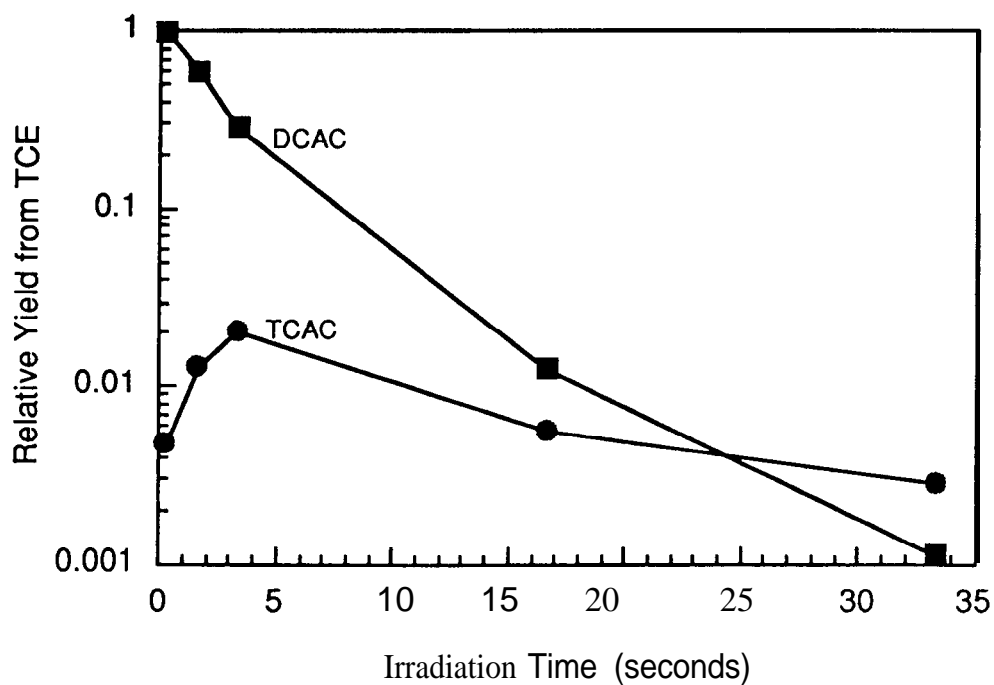


Figure 11. Product yields from the photo-oxidation of TCE in the spectrophotometer cell

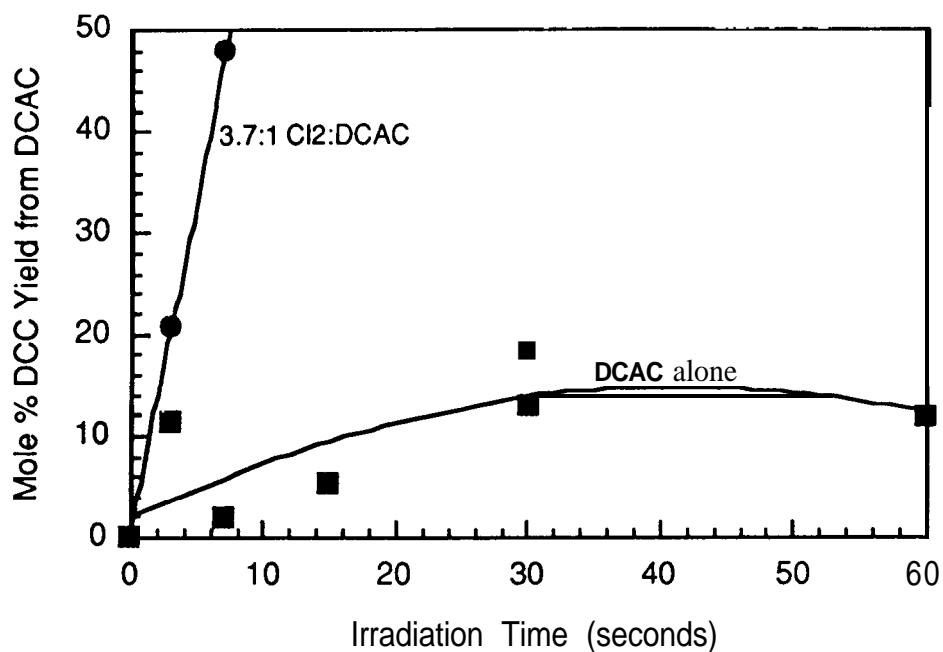
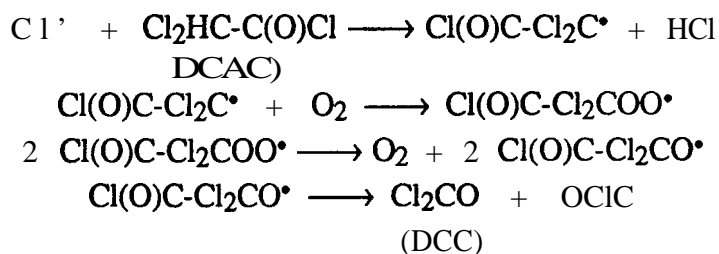
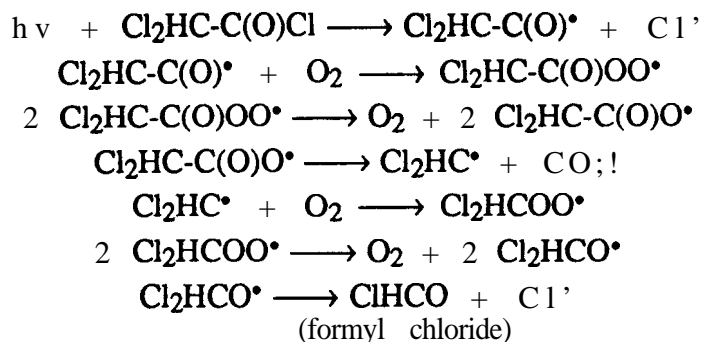


Figure 12. DCC yields from the photo-oxidation of DCAC in the spectrophotometer cell

yield increases slowly to about 15 mole % and then begins to decrease with light dose. Addition of chlorine greatly increases the DCC yield by a factor of 24 when a 3.7: 1 mole ratio of Cl_2 to DCAC is photolyzed for 7 seconds. Its formation might be caused by chlorine atom attack upon DCAC:



The low of DCC suggests that it is either photolyzed simultaneous with its production from DCAC, or that an additional DCAC reaction pathway exists that does not lead to DCC, or both. A possible additional mechanism involves photolytic cleavage of the chlorine-carbonyl bond followed by reaction with oxygen:



This mechanism predicts CO_2 and formyl chloride as the carbon-containing products. A preliminary CO_2 measurement in the 208-L pilot reactor indicated $\geq 50\%$ yield of CO_2 after 170 seconds of irradiation. Formyl chloride was not analyzed for, but it is the most likely missing product because it contains only hydrolyzable chlorine. The field data described below indicate that all of the chlorine not accounted for by DCAC is readily hydrolyzable, i.e., forms Cl^- rapidly on reaction with water. Formyl chloride hydrolyzes to give formic acid and HCl .

FIELD EXPERIMENTS

TCE disappearance data and product data from Air-2 and Air-3, are given in the Appendix. Most of the discussion will be limited to results from Air-3, because sampling conducted during the testing of Air-2 was impaired by high moisture levels in the system. Because the two principal oxidation products, DCAC and DCC, could react with water prior to sampling, they were readily lost on the reactor surface and sampling tubing. Measurements of TCE concentrations should not be influenced by this problem, however. As described in the Methods section, these difficulties were overcome before sampling for Air-3 measurements were begun.

TCE Removal Efficiency

Over the range of experimental variables covered, trichloroethene was photo-oxidized to $>99\%$ conversion except at the lowest flash frequencies and number of lamps. The tables in the Appendix give the extent of conversion under the different experimental conditions. Under the highest exposures and optimal conditions, conversions of 99.9996% were achieved. Estimation of the loss of trichloroethene was limited by the 0.01 ppmv detection limit of the gas chromatographic method.

Measured TCE Oxidation Products

Figure 13 shows the evolution of products during the photolysis of TCE in Air-3 at the field site. In order to compare total exposure levels in each reactor and to factor in flash frequency and process flow rate, a dose was calculated under each set of experimental conditions, defined as:

$$\text{Dose} = \text{Residence time} \times \text{Flash frequency} \times \text{No. of lamps} \times \text{Energy/flash} \quad (3)$$

In the case of Air-3 the dose was calculated assuming two lamps, since the flow was split off **and** sent through two reactors in series. Again, the principal organic product from the TCE photo-oxidation observed in the field studies was dichloroacetyl chloride. At the lower exposure range (1.2 kJ dose) that is just sufficient to eliminate TCE, a conversion of 86 mole % DCAC and 6.9 mole % DCC was observed in Air-3. At a dose of about 70 kJ, we found a 28 mole % conversion to DCAC and 23 mole % to DCC. As the dose was increased, by increasing either the residence time or the flash frequency, the DCAC yield fell off exponentially (Figure 13), and the DCC concentration increased. The DCC yield did not equal the DCAC loss, presumably because of concomitant DCC photolysis or other pathways for DCAC loss, as observed in the laboratory studies.

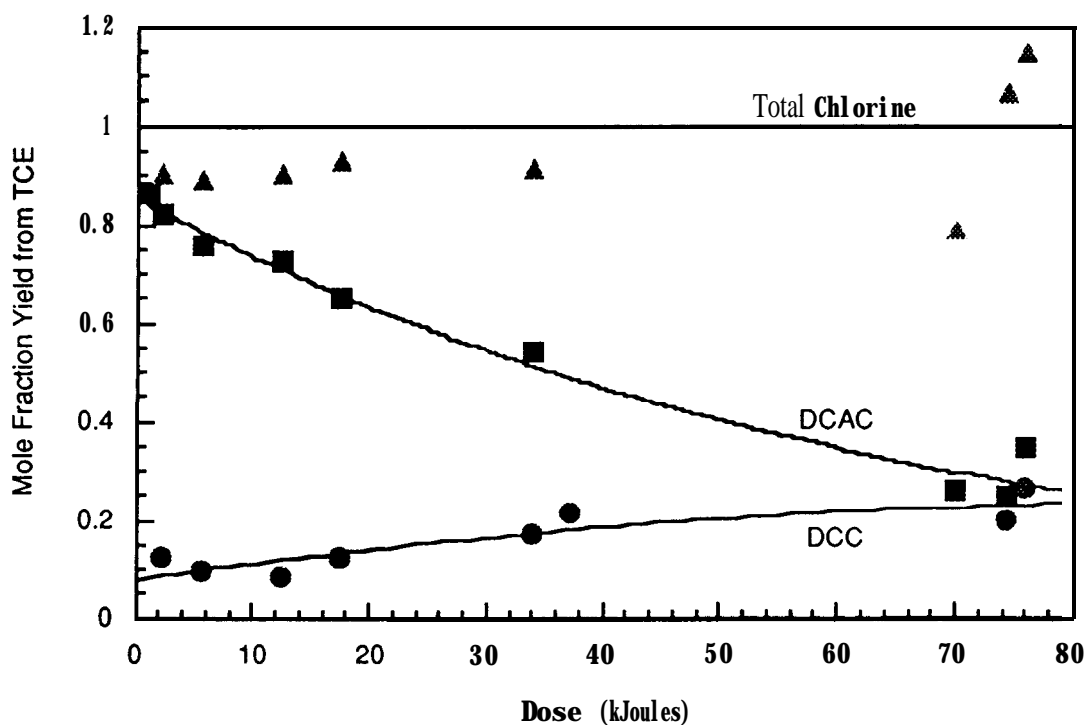


Figure 13. Product yields from the photolysis of TCE in Air-3

A mass balance for chlorine can be estimated by using the yield obtained for DCAC and the total chloride yield. If, as the evidence suggests, DCAC is the only organic product with non-hydrolyzable chlorine atoms, then the chlorine mass balance may be calculated as follows:

$$\text{Fraction chlorine recovered} = (\text{moles chloride} + 2 \times \text{moles DCAC}) / (3 \times \text{moles TCE lost}) \quad (4)$$

The chlorine recoveries taken from Air-3 ranged from 79 mole % to 115 mole % with the average about 93 ± 23 % (95% confidence interval). This high yield is constant throughout the experiment, as can be seen in Figure 1. Within the uncertainty of these measurements most of the chlorine is accounted for, indicating that all the chlorine other than one of those in DCAC is in hydrolyzable form such as in DCC or formyl chloride. The chlorine balance in Air-2 experiments was more variable due to the higher humidity, causing sampling loss, as mentioned above.

The excellent chlorine balance implies that products such as carbon tetrachloride and chloroform, which have been detected previously in TCE photo-oxidation (Huybrechts and Meyers, 1966), are present in very low yield in our system. The TO-14 whole air sampling results given in Table 2 confirm this. The chloroform yield was found to be 0.65 % of the TCE input, and the carbon tetrachloride yield 0.15%, and the methylene chloride yield 0.05%.

A mass balance for carbon cannot be determined based upon the measurements performed in this study. Potential carbon containing products from TCE photo-oxidation that were not examined in detail include CO, CO₂, formyl chloride and trichloroethylene oxide.

TABLE 2. TO-14 ANALYSIS SAMPLED ON 28 JAN 1992 AT 30 HZ FROM AIR-2

Sample	CCl ₄ (ppmv)	CHCl ₃ (ppmv)	CH ₂ Cl ₂ (ppmv)	PCE (ppmv)	TCE (ppmv)
Input	≤0.002*	<0.005	<0.050	0.150 [0.002]*	130.0 [0.002] (182) [†]
output	0.200	0.840	0.070	0.002	0.024 [0.001] (0.06)
20 ppmv Standard	<0.001	<0.001	<0.01 0	<0.001	15.0 [0.001] (18.3)

* Values in brackets or given as upper limits are detection limits. Detection limits for the output samples were the same as for the 20 ppmv standard.

[†] Values in parentheses were determined by Purus.

ESTIMATION OF PARAMETERS TO ACHIEVE RECOMMENDED TREATMENT LEVELS ATLLNL SITE 300

Because of the formation of toxic products, the efficacy of treatment at LLNL Site 300 cannot be measured simply in terms of TCE removal. Table 3 lists exposure limits for TCE **and its** photo-oxidation products, as estimated by Environ Corp., a consulting firm in Emeryville, CA (Tsai and Libicki, 1992). The estimate for DCAC assumes that this compound hydrolyzes rapidly in the environment or respiratory tract and thus has the same long-term toxicity as DCAA. It is clear from Table 3 that the major products are more toxic than TCE and thus would need to be removed by further photolysis or other post-treatment before emission to the atmosphere.

TABLE 3. EXPOSURE LIMITS FOR TCE AND ITS PHOTO-OXIDATION PRODUCTS

Chemical	Worker Exposure Limit' ($\mu\text{g}/\text{m}^3$)
TCE	26.8
DCAC	0.68
DCAA	0.68
DCC	12
c o	20.6

* Based on a lifetime cancer risk level 10^{-5}

Because the toxicity of DCAA is 40 times greater than that of TCE (Tsai and Libicki, 1992), the most DCAC one can emit is 1/4000 times the initial TCE concentration, or at most 0.025% DCAC remaining, to reach the goal of 99% reduction in initial toxicity. Similarly, the concentration of DCC would need to be less than 0.45% of the initial TCE concentration. To estimate the exposure time necessary to reach the required concentration of DCAC, an extrapolation must be made because no conditions used in this study reached these treatment goals. To do this we assume an exponential decrease with dose, as supported by the data over the parameters studied (Figures 11 and 13):

$$Y(t) = Y(o)e^{-kt} \quad (5)$$

where Y = relative concentration, k = first order rate coefficient, and t = time. Because we want to

substitute for the dose, we let dose = Intensity (kJoules/sec) x time (sec), thus:

$$Y(t) = Y(o) e^{-(k/I)D} \quad (6)$$

where D = dose and I = intensity.

Two important assumptions are made in deriving this expression. The first is that DCAC destruction is always first order, which may only be a good approximation if the mechanism for its removal is direct phdtolysis. This is not be the only possibility because preliminary experiments with added chlorine gas indicated that chlorine atom attack on DCAC can occur also. The second assumption is that DCAC is created instantly at zero time, which is a reasonable approximation when the rates of appearance and disappearance of DCAC are compared.

Table 4 gives the result of this extrapolation along with the first order rate constants obtained from the fits to three sets of data. The fit to data from Air-2 data includes only the highest yields over the dose range, because lower yields may have resulted from poor sampling recovery caused by water reactions. The data indicate that a flow rate of 13 - 20 cfm in Air-2 or Air-3 with four 3.7-kW lamps can achieve the desired DCAC reduction.

TABLE 4. TREATMENT PARAMETERS FOR 99% REDUCTION IN TOXICITY BY UV ALONE
AT LLNL SITE 300

Data Source for Extrapolation	k (sec ⁻¹)	Calculated Residence Time (seconds)	Calculated Process Flow (cfm)	TCE Input Concentration (ppmv)
30 Hz Air-3	0.128	65	15.2	30
All Air-3	0.111	74.8	13.2	30
Highest Air-2	0.0267	301	20.2	30

Insufficient data are available to determine if the DCC concentration would be low enough when the DCAC treatment goal is reached. DCC could easily be removed with a water scrubber, where it would rapidly hydrolyze to CO₂ and HCl. However, traces of DCAC would also hydrolyze to dichloroacetic acid (DCAA) and HCl and, depending on the water flow, the residual

DCAA would still be at least an order of magnitude above the proposed drinking water limit of 0.2 ppb (Bull R., University of Washington, personal communication, 1991). A relatively dry scrubber, such as slaked lime is a possibility because it would trap both DCC and DCAC. However, DCAA is likely to leach out when the lime is landfilled. Promising approaches include using very small flows of water and treating them by incineration or other thermal processes.

REFERENCES

- Atkinson R.; Aschmann S.A. ***Int. J. Chem. Kinet.* 1987,19, 1097,**
- Baulch D.L.; Cox R.A.; Hampson R.F.; Kerr J.A.; Troe J.; Watson R.T. ***J. Phys. Chem. Ref. Data* 1980,9, 295.**
- Blystone P.; Johnson M.; Haag, W.R. Advanced ultraviolet flashlamps for the destruction of organic contaminants in air, ACS Symposium Series, 1992, presented at the ACS I & EC Division Special Symposium, Atlanta, Ga., Oct 1-3, 1991.
- EG&G Publication ***Flashlamp Applications Manual* 1988.**
- Hubrich C.; Stuhl F. ***J. Photochem.* 1980, 12, 93-107**
- Huybrechts G.; Meyers L. Gas-phase chlorine-sensitized oxidation of trichloroethylene, ***Transactions of the Faraday Society*, 1966,62,2 19 1.**
- Nicole I.; De Laat J.; Dore M.; Duguet J.P.; Bonnel C. ***Water Res.* 1990,24, 157.**
- Phillips, R. ***Sources and Applications of Ultraviolet Radiation***; Academic Press, 1963.
- Rebbert R.E.; Ausloos P.J. ***J. Photochem.* 1976/77,6, 265.**
- Sanhueza E.; Hisatsune I.C.; Heicklen J. ***Chem. Rev.* 1976, 76, 801**
- Tsai P.; Libicki S. Environ Corporation Report to Purus, 1992.
- Winberry W. T.; Murphy N. T.; Riggan R. M. "Methods for Determination of Toxic Organic Compounds in Air, EPA Methods", Noyes Data Corporation, Park Ridge, New Jersey, **1990, 153.**
- Zepp R.G.; Cline D.M. ***Environ. Sci. Technol.* 1977, 11, 359.**

APPENDIX A

TABLE A-I. AIR-2 RESULTS

Freq. (Hz)	No. of Lamps	Flow (cfm)	Res. Time (sec)	[TCE] input (ppmv)	[TC E] output (ppmv)	TCE Destruction (%)	DCC Yield (ppmv)	DCAC Yield (ppmv)	Mole % DCC	Mole % DCAC	Mole Cl	Chlorine Balance (Mole %)
	4		21.0	256	4.34	98.3047	26.2	9.6	10.2	3.8	16.2	18.7
	4		23.3	138	dl	≥ 99.99	26.7	41.9	19.3	30.4	47.8	68.0
	4		30.5	144	0.082	99.94 1	33.2	4.5	23.1	3.1	28.0	30.1
	4		62.5	210	dl	≥ 99.995	186.5	29.5	88.8	14.0	61.7	71.1
	4		58.8	31.8	0.28	99.1195	4.2	0.6	13.2	1.9	28.7	30.0
	4		56.6	843	0.13	99.9846	418	4.2	49.6	0.5	75.1	75.4
	4		58.3	10600	0.038	99.9996	959	42.5	9.0	0.4	6.6	6.9
	4		58.3	182	0.06	99.96 0	112	4	61.5	2.2	76.8	78.3
	4		59.4	29.9	dl	≥ 99.97	nd	nd	nd	nd	nd	nd
	4		20.6	113	dl	≥ 99.99	13	4.5	11.5	4.0	26.3	29.0
	4		23.3	138	0.34	99.7536	15.2	36.6	11.0	26.5	34.7	52.4
	4		30.5	149	0.21	99.8591	36.1	63.7	24.2	42.8	33.5	62.0
	4		73.9	246	dl	≥ 99.995	167	60.7	67.9	24.7	42.9	59.3
	4		58.3	166	0.06	99.9639	114	5.2	68.7	3.1	57.3	59.4
	2		57.7	1575	0.06	99.9962	nd	nd	nd	nd	nd	nd
	2		57.7	78.1	dl	≥ 99.99	nd	nd	nd	nd	nd	nd
	4		57.7	1562	0.05	99.9968	nd	nd	nd	nd	nd	nd
	2		57.7	1562	0.06	99.9962	nd	nd	nd	nd	nd	nd
	4		20.6	132	dl	≥ 99.99	12.5	40.8	9.5	30.9	12.1	32.7
	4		23.3	134	0.69	99.4851	11.6	33.6	8.7	25.1	34.8	51.5
	4		30.6	167	1.9	98.8623	24.4	80.9	14.6	48.4	28.6	60.9
	4		57.7	148	0.33	99.7770	16.6	12.4	11.2	8.4	17.1	22.7
	4		56.6	113	0.41	99.6372	56.1	40.5	49.6	35.8	76.8	100.7
	4		57.7	84.9	dl	≥ 99.99	nd	nd	nd	nd	nd	nd
	2		57.7	84.9	0.87	98.9753	nd	nd	nd	nd	nd	nd
	4		57.7	1236	0.13	99.9895	nd	nd	nd	nd	nd	nd
	2		57.7	1236	27.8	97.7508	nd	nd	nd	nd	nd	nd

TABLE A-1. (CONT'D) AIR-2 RESULTS

Freq. (Hz)	No. of Lamps	Flow (cfm)	Res. Time (sec)	[TCE] input (ppmv)	[TCE] output (ppmv)	TCE Destruction (%)	DCC Yield (ppmv)	DCAC Yield (ppmv)	Mole % DCC	Mole % DCAC	Mole % Cl ⁻	Chlorine Balance (Mole %)
	4		21.3	149	23.6	84.1611	7.1	10.3	4.8	6.9	6.8	11.4
	4		23.3	149	35.1	76.4430	10.5	17	7.0	11.4	13.9	21.5
	4		31.1	115	25	78.2609	18.1	82.2	15.7	71.5	35.9	83.6
	4		53.2	147	7.9	94.6259	7.9	24.4	5.4	16.6	30.9	42.0
	4		58.8	40.2	0.96	97.6119	3.1	6.7	7.7	16.7	23.0	34.1
	4		59.4	34.8	0.37	98.9368	nd	nd	nd	nd	nd	nd
	4		61.2	773	166	78.5252	100.5	120.9	13.0	15.6	36.9	47.3
	4		56.6	109	55	49.5413	49.3	76.7	45.2	70.4	85.6	132.5
	4		58.3	3120	1330	57.3718	113	226	3.6	7.2	8.9	13.7
	4		57.7	105	22.8	78.2857	nd	nd	nd	nd	nd	nd
	2		57.7	105	31.7	69.8095	nd	nd	nd	nd	nd	nd
	4		57.7	1466	429	70.7367	nd	nd	nd	nd	nd	nd
	2		57.7	1466	596	59.3452	nd	nd	nd	nd	nd	nd

TABLE A-2. AIR-3 RESULTS

Freq, (H z)	No. of Chambers	Flow (cfm)	Res. Time (sec)	[TCE] input (ppmv)	[TCE] output (ppmv)	TCE Destruction (%)	DCC Yield (ppmv)	DCAC Yield (ppmv)	Mole % DCC	Mole % DCAC	Mole % Cl ⁻	Chlorine Balance (Mole %)
	4	103	9.6	76.4	dl	≥ 99.99	nd	20.2	nd	25.6	61.6	78.8
	4	97	10.1	108.5	dl	≥ 99.99	21.3	26.5	19.6	24.4	89.9	106.2
	4	95	10.4	98.3	dl	≥ 99.99	25.6	34	26.0	34.6	91.4	114.5
	2	106	4.6	91.7	0.07	99.92	15.9	49.2	17.3	53.7	55.3	91.1
	4	97	10.1	106.8	dl	≥ 99.99	22.8	nd	21.3	nd	68.2	nd
	2	103	4.6	101.3	dl	≥ 99.99	12.6	65.3	12.4	64.5	43.2	86.2
	4	95	10.4	104.9	dl	> 99.99	8.7	75.7	8.3	72.2	41.9	90.0
	2	103	4.6	101.4	dl	≥ 99.99	9.4	76.3	9.3	75.2	36.6	88.8
	4	106	9.3	101.7	0.65	99.16	12.5	83.2	12.3	81.8	35.8	90.3
	2	103	4.8	96.5	13.23	86.57	6.8	84.9	6.9	86.2	35.8	93.3